

Thermoelectric Properties of Cr₃S₄-Type Selenides

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Abstract

Several compounds with the Cr₃S₄ structure type have been studied for their thermoelectric properties. All exhibit low lattice thermal conductivity of about 15 mW/cmK, independent of temperature. Many of the compounds, such as Co₃Se₄, Ni₃Se₄, Fe₃Se₄, Ti₃Se₄, FeNi₂Se₄, and FeCo₂Se₄, are metals with relatively low electrical resistivity and Seebeck coefficient. The Cr containing compounds, such as Cr₃Se₄, NiCr₂Se₄, CoCr₂Se₄, and FeCr₂Se₄, have the largest Seebeck coefficients and highest resistivity. The most promising of these materials for thermoelectric applications is FeCr₂Se₄.

Introduction

The growth of commercial applications of thermoelectric devices depends primarily on increasing the figure of merit, ZT , for thermoelectric materials. The figure of merit is defined as $ZT = \alpha^2 \sigma T / \lambda$, where α is the Seebeck coefficient, σ the electrical conductivity, λ the thermal conductivity, and T is the absolute temperature. Materials with a large $\alpha^2 \sigma$ value, or power factor, are usually heavily doped semiconductors, such as Bi₂Te₃. The thermal conductivity of semiconductors is usually dominated by phonon or lattice thermal conductivity. Thus, one method for finding new, advanced thermoelectric materials is to search for semiconductors with low lattice thermal conductivity.

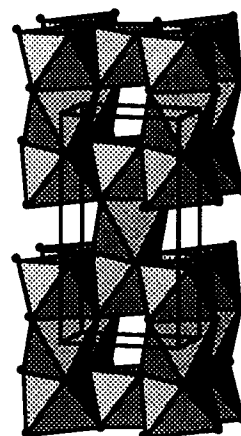


Figure 1. Illustration of the Cr₃S₄ unit cell showing S atoms as spheres and Cr atoms (not shown) at the center of the shaded octahedra. The vertical chain of face sharing octahedra is cut into segments of three units by a vacancy. The monoclinic unit cell is indicated.

In this paper we evaluate compounds based on the defect-NiAs structure, Cr₃S₄, with general composition A_xB_{3-x}X₄ where A and B are transition metals and X is a chalcogen, primarily Se. Previous work on such compounds [1] have shown that a range of metals and insulators exist with this structure type, and that they may have extremely low thermal conductivity [2, 3]. For instance, the magnetic semiconductor FeCr₂Se₄ has been reported [2-4] to have room temperature thermal conductivity of 1.1 mW/cm K which is an order of magnitude lower than the state-of-the-art thermoelectric material, Bi₂Te₃ alloys.

The structure of Cr_3S_4 (Figure 1) consists of hexagonally close packed S atoms with metal atoms in the octahedral holes as in NiAs. The metal atoms have 6 anion near neighbors (forming an octahedron) plus two nearby metal atoms along the c -axis. As suggested by Spitzer [5] the relatively high coordination number of the atoms in this structure may favor low lattice thermal conductivity. Due to the stoichiometry (three metal atoms for every 4 non-metal atoms), 1/4 of the octahedral holes must be vacant. The scattering of phonons by these vacancies should help reduce the lattice thermal conductivity.

In many defect-NiAs compounds, the defects order, increasing the unit cell size and lowering the symmetry (e.g. from hexagonal $P6_3mc$ in NiAs to monoclinic $C2/m$ for Cr_3S_4). The vacancies cut the chains of metal atoms along the NiAs c -axis into units of 3 (Figure 1). Since there are two equivalent end members of the three atom chain for every central atom, one may expect that for the composition AB_2X_4 the B atoms would occupy the end positions and the A atom the central position of the chain. However, since these two metal atom sites are nearly identical (the central site is slightly larger, due to the greater number of vacancies nearby), there can be significant mixing of different atoms on these two sites. Indeed, a full solid solution is found for many of these $\text{A}_x\text{B}_{3-x}\text{X}_4$ compounds.

There are approximately 90 known $\text{A}_x\text{B}_{3-x}\text{X}_4$ compounds with the Cr_3S_4 structure type. Many of these compounds have $\text{X} = \text{Se}$ compounds with 3-d transition metals for A and B atoms (Figure 2), and constitute most of the samples in this investigation. Several of the known AB_2S_4 sulfides with the Cr_3S_4 -type structure are high temperature/pressure polymorphs of compounds with the Spinel structure at room temperature and pressure. Known compounds with $\text{X} = \text{Te}$ are metals with low thermopower (α) (Table 1).

Known Selenide Defect NiAs																		1
1	2	AB_2Se_4																2
3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	He
Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				

Figure 2. Elements known to make $\text{A}_x\text{B}_{3-x}\text{Se}_4$ compounds with the Cr_3S_4 structure type, where A and B are metals shaded in the figure.

The Cr_3S_4 -type selenides are attractive for thermoelectric applications not only because they may have low thermal conductivity as suggested above, but they also exhibit a range of electronic properties - from metals to semiconductors. Precise, heavy doping of the semiconductor is critical to obtain optimal power factor for both n- and p-type materials. Proven thermoelectric materials such as filled Skutterudites and Zn_4Sb_3 are often difficult to dope to the optimal n- or p-type carrier concentration. An advantage of the $\text{A}_x\text{B}_{3-x}\text{X}_4$ compounds is the chemical versatility of the structure, allowing continuous doping from metal to n- and p-type semiconductor.

Experimental

The thermoelectric properties of many Cr_3S_4 compounds reported in the literature [1] were used to narrow the search. Compounds with thermopower or thermal conductivity data are summarized in Table 1.

Polycrystalline samples were prepared by mixing and reacting elemental powders in evacuated silica ampoules for several days at $700^\circ - 800^\circ \text{C}$. The samples were analyzed by x-ray diffractometry to confirm the crystalline structure. The powders were then hot-pressed in graphite dies into dense samples, 3 mm long and 12 mm in diameter. The hot-pressing was conducted at a pressure of 1400 kg/cm^2 and $700^\circ - 800^\circ \text{C}$ for about 2 hours under argon

atmosphere. The density of the samples was calculated from the measured weight and dimensions and was found to be greater than 95% of the theoretical density for all samples except those containing Ti. Pellets containing Ti or rich in Fe had many cracks and often broke apart.

Table 1. Thermoelectric properties of Cr₃S₄-type compounds found in the literature [1-4, 6-11].

Composition	ρ_{300} m Ω .cm	S_{300} μ V/K	λ_{300} mW/cmK	λ_{calcd} mW/cmK	Ref
Fe ₃ Se ₄	2	-15			9
TiFe ₂ Se ₄	0.3	40			6
VFe ₂ Se ₄	3	40			6
	1	-15	21	16	7
NiFe ₂ Se ₄	0.2	-10	29	2	7
CrFe ₂ Se ₄	5	-18	7.5	6	7
NiV ₂ Se ₄	1	-5			8
VCr ₂ Se ₄	45		4.4		3
	50	4	7		2
NiCr ₂ Se ₄	20	-21			8
	30	3.5	9	9	2
	27		5.5	5	3
FeCr ₂ Se ₄	100	48	1.1	1	2
	10	60			4
	125	25	1.1	1	3
Rh ₃ Se ₄	2.6	-15			10
Cr ₃ Te ₄	1	-12			1
FeCr ₂ Te ₄	1	2			4
CoCr ₂ Te ₄	5	-10			11

The samples were also characterized by microprobe analysis which was performed using a JEOL JXA-733 electron superprobe operating at 20 kV and 15 nA. All samples not containing Ti or V were found to have less than 1% of impurity phases. The elemental concentrations determined from microprobe analysis were within experimental uncertainty (about 1% atomic) of the expected values.

Samples in the form of disks (typically a 1.0 mm thick, 12 mm diameter slice) were cut from the cylinders using a diamond saw for electrical and thermal transport property measurements. Temperature dependence of electrical resistivity, Hall effect, Seebeck coefficient, thermal diffusivity and heat capacity measurements were conducted on selected samples between 80 and 800K. The resistivity and Hall effect were measured using

the method of Van der Pauw [12]. The carrier density was calculated from the Hall coefficient, assuming a scattering factor of 1.0 in a single carrier scheme, by $n = 1/R_H e$, where n is the density of holes or electrons, and e is the electron charge. The Hall mobility (μ_H) was calculated from the Hall coefficient and the resistivity values by $\mu_H = R_H/\rho$. Normally, the uncertainty is estimated to be $\pm 0.5\%$ and $\pm 0.2 \text{ cm}^2/\text{Vs}$ for the resistivity and mobility data, respectively. The Hall effect, however, is very small and compounded by the anomalous Hall effect because of the magnetism. Therefore it is difficult to estimate the Hall mobility or carrier concentration. The Hall mobilities shown in Table 2 equate to carrier concentrations in excess of $10^{20}/\text{cm}^3$. The Seebeck coefficient (α) was measured with a high temperature light pulse technique [13]. The error of the Seebeck measurement was estimated to be less than $\pm 3\%$. Room temperature thermal conductivity was measured using the comparison method [14]. High temperature heat capacity and thermal diffusivity were measured using a flash diffusivity technique [15]. The thermal conductivity (λ) was calculated from the experimental density, heat capacity, and thermal diffusivity values. The overall error in the thermal conductivity measurements was estimated to be about $\pm 10\%$.

Results and Discussion

The Cr₃S₄-type selenides exhibit a wide variety of electronic properties (Table 2). Many are metals (resistivity increases with temperature) having room temperature resistivity (ρ) from about 10^{-4} to $10^{-3} \Omega\text{cm}$. The non-linearities and hysteresis in the resistivity as a function of temperature may be due to magnetic or structural changes, or even loss of Se at high temperatures (Figure 6). Sample cracking at high temperature may cause some of the observed hysteresis.

Composition	Metal/ Semic.	ρ_{300} m Ω .cm	S_{300} μ V/K	μ_{H300} cm ² /Vs	λ_{300} mW/cmK	$\lambda_{lattice}$ mW/cmK
Ni ₃ Se ₄	M	0.1	-6	0	88	11
FeNi ₂ Se ₄	M	0.2	-12	0	34	7
Co ₃ Se ₄	M	0.3	-12	0	35	13
FeCo ₂ Se ₄	M	0.3	-15	0	32	15
Ti ₃ Se ₄	M	0.4	1	0.3	31	17
Fe ₃ Se ₄	M	0.7	-5	0	14	6
Cr ₃ Se ₄	M	1.1	-30	-0.9	17	12
TiFe ₂ Se ₄	S	2.0	-10	0	12	9
FeCr ₂ Se ₄	S	0.6	5	2	18	8
NiCr ₂ Se ₄	S	1.0	-28	-0.2	19	14
CoCr ₂ Se ₄	S	3.0	-32	-0.1	17	15
FeCr ₂ Se ₄	S	10.0	128	0.1	13	12

Table 2. Room temperature thermoelectric properties from this study. A Lorenz value of $1.8 \times 10^{-8} \text{ J}^2/\text{K}^2\text{C}^2$ was used to calculate the electronic contribution to the thermal conductivity.

Neither the high power factor of TiFe₂Se₄ nor the extremely low thermal conductivity values reported in the literature (Table 1) could be confirmed.

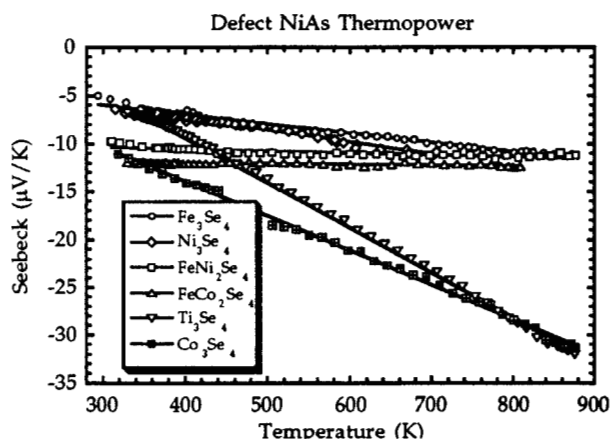


Figure 3. Thermopower of some Cr₃S₄-type metals.

The room temperature thermopower of the metals tend to be negative and have a somewhat larger magnitude than elemental metals. The Seebeck coefficient is linear with temperature, T , as expected from the diffusion thermopower. For an electron gas the diffusion thermopower is given by

$$\frac{\pi^2 k_B^2 T}{3e} \left(\frac{\partial \ln(\sigma(E))}{\partial E} \right)_{E_F} \quad [16]. \quad \text{The linear}$$

extrapolation of the thermopower to a non-zero value may be due to the phonon drag component to the thermopower [17].

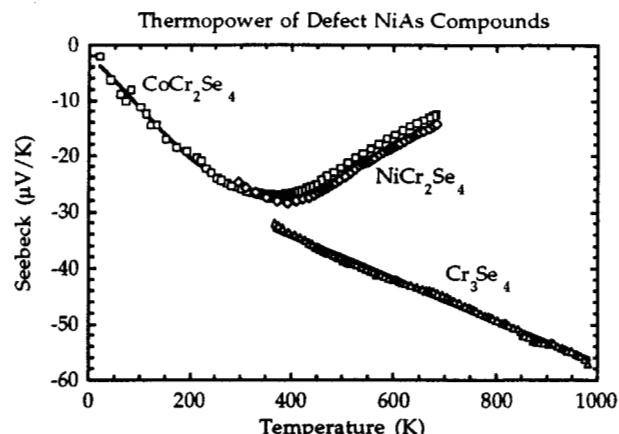


Figure 4. Thermopower of some Cr containing Cr₃S₄-type compounds.

Other Cr₃S₄-type selenides, typically samples with Cr³⁺ are semiconductors where the resistivity decreases with temperature. Many of these semiconductors have low activation energies and low room temperature resistivity. This translates into a small bandgap and high carrier concentration.

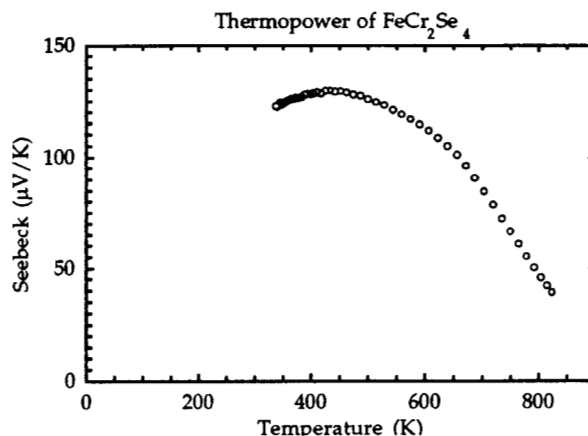


Figure 5. Thermopower of FeCr₂Se₄.

CoCr₂Se₄ and NiCr₂Se₄ are low band gap semiconductors (0.02 eV) with maximum Seebeck at about 350K. FeCr₂Se₄ is more semiconducting (0.04 eV activation energy at room temperature) with maximum Seebeck at 440K.

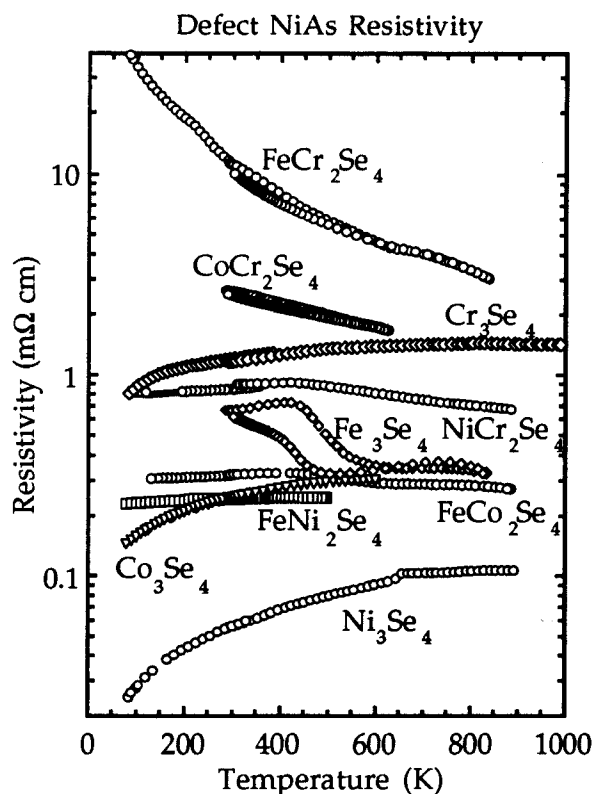


Figure 6. Electrical resistivity of Cr_3S_4 -type selenides.

Exchange split Cr^{+3} in octahedral coordination will have 3 electrons to completely fill the majority spin T_{2g} orbital (or subsequent band); thus Cr^{+3} may not provide metallic carriers. However, Co^{+2} which has 7 d electrons must have a partially filled orbital. Thus CoCr_2Se_4 should be a metal. However, if these electrons are localized on the Co atoms, which are relatively distant from one another, electron conduction may not be metallic but proceed by a (small polaron) hopping mechanism. Such a compound can also be considered a Mott insulator. If CoCr_2Se_4 is a Mott insulator, then NiCr_2Se_4 and FeCr_2Se_4 are likely Mott insulators for similar reasons.

The resistivity due to small polaron hopping conduction has only a slightly different temperature dependence ($T \exp(E_a/kT)$) than that expected of a semiconductor ($\mu^{-1} \exp(E_a/kT)$ where the mobility μ is proportional to $T^{-3/2}$ for many semiconductors). Both forms are dominated by an exponential

with characteristic energy E_a . For the materials described here the resistivity data is not sufficiently well described by either of the exact forms to determine the transport mechanism. Nevertheless, band semiconductor transport characteristically has carriers with high mobility and low concentration while small polarons have high concentration and low mobility. Thus, the data suggests that these materials have polaron conductivity.

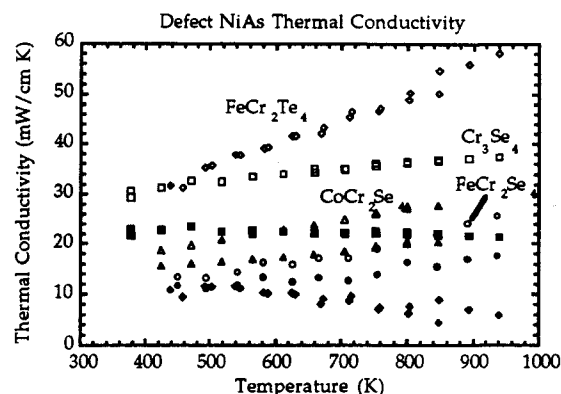


Figure 7. Thermal conductivity (open symbols) and lattice contribution, calculated using the Lorenz factor typical for metals, of Cr_3S_4 -type compounds (filled symbols).

The thermal conductivity λ is given by the sum of the electronic λ_E and lattice contributions λ_L . λ_E is directly related to the electronic conductivity: $\lambda_E = L\sigma T$, where L is the Lorenz factor. A Lorenz factor of $1.8 \times 10^{-8} \text{ J}^2/\text{K}^2\text{C}^2$ gives consistent room temperature lattice thermal conductivity values for the compounds listed in Table 2. If the Lorenz factor typical for metals ($2.4 \times 10^{-8} \text{ J}^2/\text{K}^2\text{C}^2$; see Figure 7) were used, the calculated electronic contribution would be greater than the measured total thermal conductivity. The anomalously low lattice thermal conductivity calculated for FeCr_2Te_4 at high temperatures further indicates a lower than expected Lorenz factor (Figure 7). The low Lorenz factor may

indicate significant electron-electron scattering ([18] p109).

The lattice thermal conductivity is relatively independent of temperature (Figure 7) indicating multiple scattering processes. Low, temperature independent thermal conductivity is found in complex structures such as glasses. Common crystalline materials have large lattice thermal conductivity that is proportional to $1/T$. The ternary Cr_3S_4 -type compounds have lower lattice thermal conductivity as is often observed for such alloying.

The power factor and therefore figure of merit is very low for most of these compounds. This may be traced to the very low Hall mobilities. Typical thermoelectric materials have Hall mobilities greater than $10 \text{ cm}^2/\text{Vs}$, whereas the materials in Table 2 have mobilities at least 10 times less. This may be due to the hopping method of transport, the increased electron scattering from the transition metal magnetic moments (magnon scattering) or due to the lower covalency of these materials as compared to conventional thermoelectric semiconductors.

The best thermoelectric compounds studied here contain chromium and selenium. Chromium selenide, Cr_3Se_4 , has the highest power factor of the metals and the largest apparent Hall mobility. The semiconductor with highest Seebeck coefficient is FeCr_2Se_4 . The solid solution $\text{Fe}_x\text{Cr}_{3-x}\text{Se}_4$ was therefore chosen for further study to determine the optimal thermoelectric properties.

Summary

A variety of Cr_3S_4 -type compounds were examined for high thermoelectric figure of merit. Reported thermoelectric properties and the existence of known compounds helped guide the selection of materials to reexamine. All showed low, glass-like thermal conductivities. The Tellurium containing compounds were eliminated due to their low Seebeck coefficients. The selenides show a

variety of electronic properties from metals to small polaron semiconductors, all with very low mobilities. The most promising compound studied is $\text{Fe}_x\text{Cr}_{3-x}\text{Se}_4$ since it is the most semiconducting and can easily be doped by changing x .

Acknowledgments

We would like to thank A. Zoltan, L. D. Zoltan, S. Chung, and A. Borshchevsky for their help on this project. This work was carried out at the Jet Propulsion Laboratory-California Institute of Technology, under contract with NASA and supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E407.

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